EXCITED ELECTRONIC STATES USING GAMESS

LEVELS OF THEORY

- Singles CI
  - All single excitations from RHF ground state
  - Brillioun Theorem: $\langle \Psi_0 | H | \Psi_i^a \rangle = 0$
    - No improvement of ground state
  - Simplest level of theory for excited states
  - Accuracy ~ Hartree-Fock
  - Best for lowest lying excited states
  - Fails for states dominated by double excitations
    - Common for higher excited states

SINGLES CI

- In GAMESS
  - $CONTRL CITYP=CIS …$END
  - $CIS
    - NSTATE=(# of states requested)
    - ISTATE=(choose one)
    - MULT=(spin multiplicity)
    - CISPRP={.T., .F.}
      - Generates properties for ISTATE
      - Requires calculation of density matrix
  - Can do geometry opts using analytic gradients

LEVELS OF THEORY

- CISD
  - All single and double excitations from RHF ground state
  - Much more accurate than CIS
  - Much more time-consuming than CIS
    - Requires (vv|oo) and (vo|vo) integrals
  - Analytic gradients available
    - Very time-consuming

CISD

- In GAMESS
  - $CONTRL CITYP=GUGA …$END
  - $CIDRT
    - GROUP= (point group or subgroup)
    - IEXCIT=2 (CISD)
      - This will generate all single and double excitations
    - Can reduce the computational effort using
      - NFZV= (# omitted virtuals)
      - Not systematic

LEVELS OF THEORY

- EOM-CC
  - Equations of motion (EOM) coupled cluster
  - Calculates excitation energies directly
    - More accurate than subtracting excited - ground state
  - Much more accurate than CIS
    - Options include EOM-CCSD(T), CR-EOM-CCSD(T)
    - Starting wave function can come from CIS or CISd
      - Small d means identify active space for doubles
  - Much more time-consuming than CIS or CISD
  - No analytic gradients

EOM-CC

- In GAMESS
  - $CONTRL CCTYP=EOM-CCSD …$END
  - $EOMINP
    - GROUP= (point group or subgroup)
    - MTRIP=
      - Method for triples
        - » 1=CR-EOMCCSD(T) standard
        - » 2=CR-EOMCCSD(T) iterative CISD starting point
        - » See manual for other options
    - MINIT=
      - Initial guess procedure for EOM procedure
        - » 1=CISd (see manual for options)
        - » 2=CIS

LEVELS OF THEORY

- Multi-reference CI
  - CI on top of MCSCF
    - FOCI (first order CI): All single excitations from each MCSCF determinant
    - SOCI (second order CI): All single & double excitations from each MCSCF determinant
    - Better than CIS or CISD since orbital space is re-optimized in MCSCF step

MRCI

- In GAMESS
  - Assume MCSCF was done in previous run, orbitals have been checked and read in using $VEC
  - $CONTRL CITYP=GUGA
  - $CIDRT
    - GROUP= (point group or subgroup)
    - FOCI=.T. or SOCI=.T.

COMING TO GAMESS

- Time-dependent density functional theory (TDDFT)
  - Similar approach to EOM-CC
  - Similar level of theory to CIS, except based on DFT
    - Single excitations from Kohn-Sham determinant
    - More accurate than CIS since DFT better than HF
    - Fails for states dominated by double excitations
    - Like DFT, tough to predict success or failure

ISSUES FOR PHOTOCHEMISTRY

- Many excited electronic states of various spins
  - Surface crossings are common
    - Different spin states: intersystem crossings
      - Spin-orbit coupling (SOC) can be important
      - Several SOC methods in GAMESS
        - » Full all-electron (Breit-Pauli)
        - » Partial two-electron (P2E)
        - » One-electron Z_{eff} method
    - Same spin states
      - Born-Oppenheimer breakdown
      - Derivative (vibronic) coupling important
  - Both lead to radiationless transitions
  - Essential processes in photochem, photobiology